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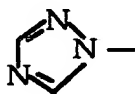
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(54) **Aquatic antifouling compositions.**

(57) An aquatic antifouling composition having low toxicity and pollution risks is described, comprising an aquatic antifouling composition comprising at least one compound possessing a 1,2,4-triazole group represented by the general formula:



at least one insoluble dithiocarbamic acid derivatives possessing a dithiocarbamyl group



and optionally an organic or inorganic copper compound

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This invention concerns an aquatic antifouling composition useful for reducing or preventing damage to ship hulls, fishnets such as nursery nets and stationary nets, and other marine structures, caused by marine organisms which adhere to underwater surfaces.

Ships, specifically their bottoms and waterline zones, fishnets such as nursery nets and stationary nets, and other marine structures are subject to adhesion of marine organisms such as barnacles, hydroids, ascidians, hard-shelled mussels and oysters, algae such as sea lettuce, green laver and marine-spirogyra, and various bacteria, moulds and diatoms called slime. Their adhesion can have a serious effect.

In the case of a ship, for example, a several percent increase in the resistance of the hull due to the adhesion of marine organisms causes a decrease in speed and reduction in fuel efficiency.

Stationary structures exposed to sea water, for example, structures for harbour facilities such as nautical beacons, floating beacons, mooring buoys, floating piers, floating breakwaters, and floating docks, pipelines, bridges, tanks, water pipes in power stations, seashore industrial plants, mooring ships, mooring and floating fishing structures, fish preserving structures, and stationary nets and other structures for fishing facilities, suffer various kinds of damage such as corrosion, sinking due to increased weight, and loss of balance, all caused by adhesion of marine organisms such as those described above.

At industrial facilities and power stations located along seashores which use sea water for cooling or for other purposes, marine organisms adhere to seawater inlets and outlets, and coastal structures such as channels and culverts. The volume occupied by the organisms at times reaches the order of some tens of percents of the internal volume of tubular structures, thus causing a decrease in the available cross-sectional area of waterways and an increase in the resistance to the liquid flow. Blockage of filter screens used to remove suspended solids is also a serious problem.

Fishnets such as nursery nets and stationary nets and marine ropes are subject to adhesion of organisms such as barnacles, hydroids, ascidians, green lavers and brown lavers. Great expense is required for removal of these organisms and repair or repainting of the structures.

Heretofore, the protection of marine structures from the adhesion of marine organisms ("biofouling") has been accomplished using sparingly soluble inorganic copper compounds, organic tin compounds, organic tin polymers, or organic nitrogen-sulphur compounds.

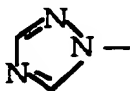
These compounds have various drawbacks however, including toxicity, pollution and in some cases failure to maintain sufficient effect when used for a long time as an aquatic antifoulant. For example, organic tin compounds are highly effective in preventing the adhesion of marine organisms, and they have been regarded as efficient antifouling components and widely used. Recently however, drawbacks of these organic tin compounds — low rate of degradation, accumulation in living bodies, toxicological problems, risk of environmental pollution — have been drawing attention.

Like organic tin compounds, dithiocarbamates which are organic sulphur compounds are also widely used as antifouling components. For example, Japanese Unexamined Patent Publication No. Sho 51-49227 discloses that biofouling is inhibited by coating fishnets with a composition obtained by combining manganese ethylenedisithiocarbamate as an antifouling component with a carrier. Also, Japanese Unexamined Patent Publication No. Sho 51-51517 discloses an antifouling composition for fishnets comprising a heavy metal salt of ethylenedisithiocarbamic acid, a cellulose resin and a carrier.

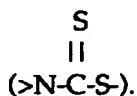
As antifouling agents organic tin compounds represented by tributyltin hydroxide, triphenyltin hydroxide and the like, tin-containing copolymers of such monomers as tributyltin (meth)acrylate, triphenyltin (meth)acrylate, bis(tributyltin)fumarate and the like, and tin-containing copolymers comprising those monomers and vinyl monomers are considered most desirable in terms of retention of efficacy and stability of effect. However, their use is now very much undesirable because of their toxicity and pollution problems.

From an environmental point of view, metal salts of dithiocarbamic acid are generally regarded as being among the most desirable active components for antifouling agents. In many cases, however, retention of efficacy and stability are not satisfactory. In order to solve these problems, a heavy metal salt of an alkylenedisithiocarbamic acid may be combined with an inorganic copper compound to provide an antifoulant component, and some other antifouling agents such as organic tin compounds may be added to the combination. Even this, however, is not always satisfactory.

The present invention provides an aquatic antifouling composition comprising at least one compound possessing a 1,2,4-triazole group represented by the formula:



and at least one insoluble dithiocarbamic acid derivative possessing a dithiocarbamyl group

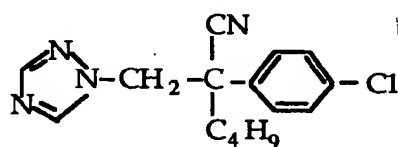


Optionally said composition may additionally comprise one or more organic or inorganic copper compounds.

In a further aspect, the invention provides a method of preventing or inhibiting the growth of marine organisms on an underwater surface susceptible or subject thereto, comprising incorporating onto the surface an effective amount of a composition according to any preceding claim.

Another aspect of the invention comprises the use of a composition as defined above to prevent or inhibit the growth of marine organisms on underwater surfaces.

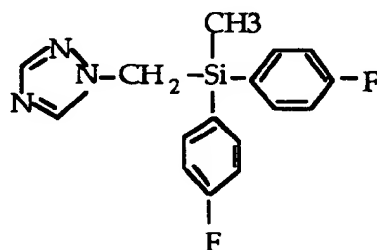
Preferred compounds possessing the 1,2,4-triazole group are:



myclobutanil; Systhane

(1)

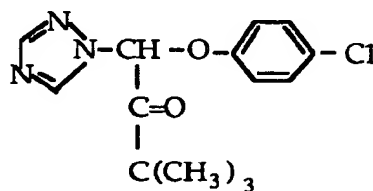
$\alpha$ -butyl- $\alpha$ -(4-chlorophenyl)-1H-1,2,4-triazole-1-propanenitrile



(2)

Flusilazole

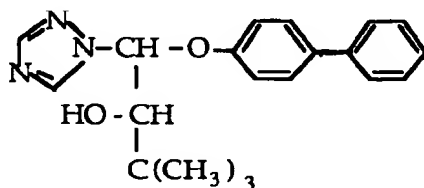
di (4-fluorophenyl)-(1,2,4-triazole-2-ylmethyl) methylsilane



(3)

Triadimefon

1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanone

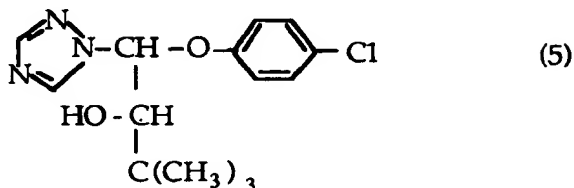


(4)

Baycor

1-(biphenyl-4-oxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanol

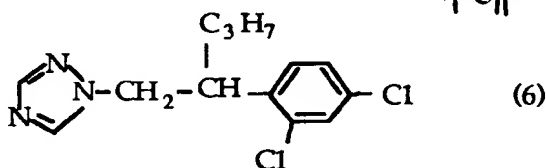
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1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanol

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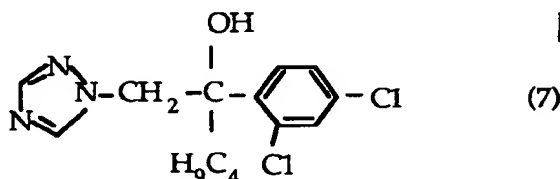


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*pefonazole*

1-(2,4-dichlorophenyl)-1H-1,2,4-triazole

25



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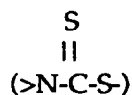
*Hexaconazole*

α-butyl-α-(2,4-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol

It should be noted that the triazole compounds are not limited to those listed above.

Specific examples of the insoluble dithiocarbamic acid derivative possessing the dithiocarbamyl group

40



include: tetra lower alkylthiuran sulphide compounds, heavy metal salts of lower alkylene-bisdithiocarbamic acids, metal-complexed heavy metal salts of lower alkylenebisdithiocarbamic acids, heavy metal salts having lower alkylenebisdithiocarbamic acids bonded to monofunctional lower alkylidithiocarbamic acids through the medium of a heavy metal, and mixtures of the foregoing metal salts.

Examples of tetra lower alkylthiuran sulphide compounds are thiram mono-or di-sulphides of tetra lower alkyl compounds such as tetramethyl, tetraethyl, tetrapropyl, tetraisopropyl and tetrabutyl compounds.

Examples of heavy metal salts of a lower alkylene-bisdithiocarbamic acid are: divalent and higher heavy metal (zinc, manganese, copper, iron, and nickel) salts of ethylenebisdithiocarbamic acid, linear or branched propylenebisdithiocarbamic acid, linear or branched butylenebisdithiocarbamic acid, N-substituted ethylenebisdithiocarbamic acid, N,N'-substituted ethylenebisdithiocarbamic acid, and N,N'-substituted butylenebisdithiocarbamic acid.

The heavy metal salts of metal-complexed lower alkylene-bisdithiocarbamic acids are those which are obtained by coordinating other metal atoms in the aforementioned heavy metal salts of lower alkylenebisdithiocarbamic acids. Representative examples include zinc-complexed manganese ethylenebisdithiocarbamate.

Examples of the heavy metal salts of a monofunctional lower alkylidithiocarbamic acid are: divalent and

higher heavy-metal (zinc, manganese, copper, iron, and nickel) salts of methylthiocarbamic acid, dimethylthiocarbamic acid, ethylthiocarbamic acid, diethylthiocarbamic acid, propylthiocarbamic acid, dipropylthiocarbamic acid, butylthiocarbamic acid, and dibutylthiocarbamic acid.

Additionally, as examples of a further kind of dithiocarbamate type compound useful in the present invention are those metal salts which are formed by combining lower alkylenebisdithiocarbamic acids and monofunctional lower alkylthiocarbamic acids through the medium of a heavy metal. They are produced by preparing mixed aqueous solutions of water-soluble salts of lower alkylenebisdithiocarbamic acids and water-soluble salts of monofunctional lower alkylthiocarbamic acids and subjecting the mixed solutions to double decomposition with a water-soluble heavy metal salt. The most typical example of this dithiocarbamate type compound is the mixed salt, bisdimethylthiocarbamoyl-zinc-ethylenebisdithiocarbamate obtained by combining ethylenebisdithiocarbamic acid and dimethylthiocarbamic acid through the medium of zinc. Generally, the products of this combination contain zinc dimethylthiocarbamate, a heavy metal salt of a monofunctional lower alkylthiocarbamic acid, and zinc ethylenebisdithiocarbamate, a heavy metal salt of a lower alkylenebisdithiocarbamic acid. These products are generally referred to as "polycarbamate agents".

The dithiocarbamate type compounds of the present invention can be used in the form of physically mixed metal salts, or in the form of chemically mixed metal salts as described above.

Specific examples of the organic or inorganic copper compound which may also be employed in compositions according to the present invention, include basic copper carbonate, basic copper chloride, copper (II) chromate, copper (II) citrate, copper (II) ferrocyanate, copper (II) fluoride, copper (II) hydroxide, copper (II) quinoline, copper-8-hydroquinoline, copper (II) oleinate, copper (II) oxalate, copper (II) oxide, copper (II) tartrate, copper (II) tungstate, copper (I) bromide, copper (I) iodide, copper (I) oxide, copper (I) sulfide, copper (I) sulphite, copper (I) thiocyanate, and copper naphthenate. One or more kinds of these compounds may be used.

The proportion of the 1,2,4-triazole compound in the aquatic antifouling composition of the present invention is preferably 50 weight % or less, more preferably 45 to 0.1 weight %. The amount of the dithiocarbamic acid derivative(s) is preferably 60 weight % or less, more preferably 55 to 0.1 weight %. The amount of copper compound(s) is preferably 60 weight % or less, more preferably 50 to 1 weight %.

Proportions of active components greater than the above upper limits can lead to difficulties in coating. Proportions below the lower limits, however, may have insufficient antifouling activity.

The aquatic antifouling composition of the present invention may be used in combination with other additives such as organic or inorganic colouring pigments, conventional paints, extenders, suspending agents, anti-dripping agents, levelling agents, colour fixing agents and UV absorbents.

It is also possible to use the aquatic antifouling composition of this invention in combination with conventional antifoulants; for example, phthalimide type compounds such as trichlorophthalimide and the like, nitrile type compounds such as 2,4,5,6-tetrachloro-1,3-isophthalonitrile (Daconile) and the like, triazine type compounds such as 2-methylthio-4-t-butylamine-6-cyclopropylamino-S-triazine (Irgarol 1051) and the like, and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Zincipridion) and the like.

The aquatic antifouling composition of this invention may also be used in combination with natural resins such as rosin or rosin ester, acrylic type resins, alkyd type resins, epoxy type resins, vinyl type resins, vinyl chloride type resins and so forth.

Solvents which are useful for the aquatic antifouling composition of the invention include xylene, toluene, solvent naphtha, methyl isobutyl ketone, methyl ethyl ketone, cellosolve and the like.

The antifouling composition of the present invention provides excellent efficacy in preventing the adhesion to underwater structures of a wide variety of harmful organisms including barnacles, hydroids, ascidians, sea mussels and mussels; algae such as sea lettuce, green lavers, marine-spirogyras; and various bacteria, fungi, and diatoms collectively called "slime". The antifouling effect is maintained for a substantial period of time.

It has been known that dithiocarbamate compounds are highly effective in controlling bacteria and algae, but relatively ineffective against barnacles, hydroids, sea mussels, mussels and the like. The antifouling composition of the present invention, however, has antifouling effect against a wide variety of aquatic creatures, in addition to bacteria and algae.

The antifouling composition of the invention can be used in the same manner as conventional antifouling compositions. On ship-bottoms and marine structures, for example, it may be mixed with conventional coating materials or the like, and the mixture coated on the surface by conventional coating methods. Ropes and fishnets are dipped in the prepared antifouling composition, withdrawn from the composition, and then dried.

The antifouling composition of the invention has a particularly good antifouling effect when compared with conventional organic tin type antifouling compositions. However it has a very low toxicity and risk of pollution.

(Examples )

Testing Example 15 Test for Ship-bottom Antifouling Paints

Steel panels (300 x 100 x 2 mm) which had been given sandblast treatment were painted with Zinc Shop Primer once, with Vinyl Ship-bottom No.1 Paint three times, and finally with one of the newly prepared ship-bottom antifouling paints shown in Tables 1 and 2 below three times. Then, they were dried for three days.

10 The test panels thus obtained were hung on rafts which had been located at about 2 km offshore in Uragami Bay, Nachi Katsuura, Wakayama Prefecture, Japan. The panels were dipped in the sea 1.5 m below the surface. Then, the degree of adhesion of marine organisms was observed for 30 months.

For the evaluation of effect, the following scale based on the area of adhesion (%) was used. The test results are shown in Table 2.

15

	<u>Scale</u>	<u>Area of Adhesion of marine organisms</u>
20	0	No adhesion
	1	5% or less
	2	10% or less
25	3	25% or less
	4	50% or less
	5	more than 50%
30		
35		
40		
45		
50		
55		



Table 1 (cont'd)

Examples	Concrete Example												Comparative Example										
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11
Components	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11
Vinyl acetate-vinyl chloride copolymer/VVHH	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Rosin	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Barium sulfate	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
Tricresyl phosphate	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Iron oxide red																							
Organic bentonite																							
Anti-dripping agent	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	4	4	4	4	4	4	4
Xylene	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Methyl isobutyl ketone	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	13	19	
Tributyl tin methacrylate copolymer																							18



5 Table 2Evaluation of Area adhered by Marine Organisms

10	No. of							
	<u>Months passed</u>		<u>6</u>	<u>12</u>	<u>18</u>	<u>24</u>	<u>30</u>	
15	Example	1	0	0	0	0	1	
		2	0	0	0	1	2	
		3	0	0	0	1	2	
		4	0	0	0	0	1	
		5	0	0	0	1	2	
		6	0	0	0	1	2	
		7	0	0	0	0	1	
		8	0	0	0	1	2	
		9	0	0	0	1	2	
		10	0	0	0	0	1	
		11	0	0	0	1	2	
		12	0	0	0	1	2	
30	Comparative Example	1	0	0	1	2	2	
		2	0	0	1	2	3	
		3	0	1	2	2	3	
		4	0	0	1	2	3	
		5	0	1	2	3	3	
		6	0	1	2	3	4	
		7	0	1	2	3	4	
		8	0	1	2	2	3	
		9	0	1	2	3	4	
		10	0	1	2	3	4	
		11	0	0	1	1	2	
40	No Treatment		5	5	-	-	-	

45

Testing Example 250 Test for Fishnet Antifoulants

55 Polyethylene knotless nets (5 knots 400 denier/70 pieces) were dipped in the fishnet antifoulants whose compositions are shown in Table 3. After natural drying, the nets were hung on rafts which had been located at about 2 km offshore in Uragami Bay, Katsuura, Wakayama Prefecture, Japan, and dipped in the sea 1.5 m below the surface. Then, the state of adhesion of marine organisms was observed for 6 months. The test results are shown in Table 4.

**Scale for Evaluation**

- A:** No adhesion of marine organisms.  
**B:** Some adhesion is observed, but the net can stand continuous use.  
**5 C:** Fairly large volume of adhesion and the net is unfit for continuous use.  
**D:** Considerable volume of adhesion.

**10**

**15**

**20**

**25**

**30**

**35**

**40**

**45**

**50**

**55**

**Table 3**

(Unit: weight %)

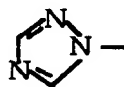
Examples	Concrete Example				Comparative Example			
	13	14	15	16	12	13	14	15
Components								
Compound possessing 1,2,4-triazole group: Compound (1) Compound (3)	10	10	10	10	15			
Polycarbonate	5		5					
Manganese salt of ethylenedisithiocarbamic acid	5		5		15			
Basic copper chloride					15			
Acrylic resin	15	15	15	15	15	15	15	15
Xylene	68	68	68	68	68	68	68	68
Anti-dripping agent	2	2	2	2	2	2	2	2
Triphenyl tin fluoride					15			

**Table 4****Evaluation of Area adhered by Marine Organisms**

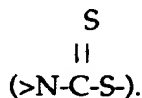
No. of Months passed		1	2	3	4	5	6
Example	13	A	A	A	A	B	B
	14	A	A	A	A	B	B
	15	A	A	A	A	B	B
	16	A	A	A	A	B	B
Comparative Example	12	A	B	B	B	C	C
	13	A	A	B	B	C	D
	14	A	A	B	C	C	D
	15	A	A	A	B	B	C
No Treatment		D	D	-	-	-	-

**Claims**

1. An aquatic antifouling composition comprising at least one compound possessing a 1,2,4-triazole group represented by the formula:



and at least one insoluble dithiocarbamic acid derivative possessing a dithiocarbamyl group



2. Composition according to claim 1, further comprising one or more organic or inorganic copper compounds.
3. Composition according to claim 1 or 2 wherein the triazole compound is a-butyl-a-(4-chlorophenyl)-1H-1,2,4-triazole-1-propan, di(4-fluorophenyl)-(1,2,4-triazole-2-ylmethyl) methylsilane, 1-(4-chlorophenyl)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanone, 1-(biphenyl-4-oxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-

butanol, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanol, 1-(2,4-dichloropropyl phenethyl)-1H-1,2,4-triazol , or  $\alpha$ -butyl- $\alpha$ -(2,4-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol.

4. Composition according to any preceding claim wherein said insoluble dithiocarbamic acid derivative is a tetra lower alkylthiuram sulphide, a heavy metal salt of an optionally metal-complexed lower alkylene-bisdithiocarbamic acid, a heavy metal salt of a monofunctional lower alkylidithiocarbamic acid, or a heavy metal salt having a lower alkylene bisdithiocarbamic acid bonded to a monofunctional lower alkylidithiocarbamic acid through a heavy metal.
5. Composition according to claim 4 wherein said heavy metal salt of a lower alkylene bisdithiocarbamic acid is a divalent or higher heavy metal (zinc, manganese, copper, iron, and nickel) salt of ethylenebisdithiocarbamic acid, linear or branched propylenebisdithiocarbamic acid, linear or branched butylenebisdithiocarbamic acid, N-substituted ethylene-bisdithiocarbamic acid, N,N'-substituted ethylenebisdithiocarbamic acid, or N,N'-substituted butylenebisdithiocarbamic acid.
6. Composition according to claim 4 wherein the heavy metal salt of a metal-complexed lower alkylene-bisdithiocarbamic acid is zinc-or-copper-complexed manganese ethylene bisdithiocarbamate.
7. Composition according to claim 4 wherein said heavy metal salt of a monofunctional lower alkylidithiocarbamic acid is a divalent or higher heavy-metal (zinc, manganese, copper, iron, and nickel) salt of methylidithiocarbamic acid, dimethylidithiocarbamic acid, ethylidithiocarbamic acid, diethylidithiocarbamic acid, propylidithiocarbamic acid, dipropylidithiocarbamic acid, butylidithiocarbamic acid, and dibutylidithiocarbamic acid.
8. Composition according to claim 4 wherein said heavy metal salt having a lower alkylene bisdithiocarbamic acid bonded to a monofunctional lower alkylidithiocarbamic acid through a heavy metal is bisdimethyl-dithiocarbamoyl-zinc-ethylenebisdithiocarbamate.
9. Composition according to any of claims 4 to 8 wherein the tetra lower alkylthiuram sulphate is a mono-or disulphide of tetramethyl, tetraethyl, tetrapropyl, tetraisopropyl or tetrabutyl compound.
10. Composition according to any preceding claim wherein said copper compound is basic copper carbonate, basic copper chloride, copper (II) chromate, copper (II) citrate, copper (II) ferrocyanate, copper (II) fluoride, copper (II) hydroxide, copper (II) quinoline, copper-8-hydroquinoline, copper (II) oleinate, copper (II) oxalate, copper (II) oxide, copper (II) tartrate, copper (II) tungstate, copper (I) bromide, copper (I) iodide, copper (I) oxide copper (I) sulfide, copper (I) sulphite, copper (I) thiocyanate, or copper naphthenate.
11. Composition according to any preceding claim wherein the triazole compound is present in an amount of up to 50%, preferably 0.1 to 45% by weight; the dithiocarbamic acid derivative is present in an amount of up to 60%, preferably 0.1 to 55% by weight; and the copper compound, if present, is in an amount of up to 60%, preferably 1 to 50% by weight.
12. Method of preventing or inhibiting the growth of marine organisms on an underwater surface susceptible or subject thereto, comprising incorporating onto the surface an effective amount of a composition according to any preceding claim.
13. Use of a composition according to any of claims 1 to 11 to prevent or inhibit the growth of marine organisms on underwater surfaces.



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 91310302.4
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	<u>EP - A - 0 135 854</u> (BAYER AG) * Claims; examples * ---	1, 5	C 09 D 5/16 A 01 N 43/647 A 01 N 47/14
X	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 13, no. 3, January 6, 1989 THE PATENT OFFICE JAPANESE GOVERNMENT page 153 C 557 * Kokai-no. 63-216 805 (HOKKO CHEM. IND. CO. LTD.) * ---	1, 5	
Y	<u>US - A - 4 542 146</u> (VAN GESTEL et al.) * Claims; examples * ---	1, 2	
Y	DATABASE WPIL no. 86-248 807 DERWENT PUBLICATION LTD., London, GB & JP-A-61-176 671 (TOKZ) 1986-08-08 -----	1, 2	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C 09 D 5/00 A 01 N 43/00 A 01 N 47/00
The present search report has been drawn up for all claims			
Place of search <b>VIENNA</b>		Date of completion of the search <b>21-02-1992</b>	Examiner <b>PAMMINGER</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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